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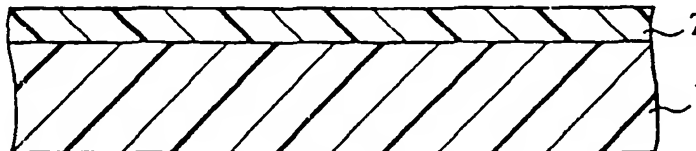
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(54) Title: FLUORINE-CONTAINING RELEASING SHEET AND PROCESS OF PRODUCTION OF SAME

(57) Abstract

Problem: to provide a releasing sheet coated with a cured material of a fluorine-containing monomer with an extremely low surface energy. Means for solution: a compound for increasing the surface



tension is added to a fluorine-containing monomer having a surface tension of not more than 25 dyne/cm to be coated on the surface of a substrate such as a polyester film or a specific substrate is used to improve the wettability of the fluorine-containing monomer with the substrate and the surface of the substrate is irradiated by an electron beam and the electron beam is irradiated under predetermined conditions. The bonding force of the substrate and releasing layer is one where there is no transfer of a releasing agent to a pressure sensitive adhesive contacting the releasing agent in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70° C and a pressure of 20 g/CM² for 24 hours.

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FLUORINE-CONTAINING RELEASING SHEET AND PROCESS OF PRODUCTION OF SAME

DETAILED DESCRIPTION OF THE INVENTION

5 Technical Field of the Invention

The present invention relates to a releasing sheet such as a releasing paper or releasing film coated with a cured material layer of a fluorine-containing monomer with an extremely low surface energy and to a process of production of the same. More particularly, it relates to a releasing sheet superior in adhesion between a polyester or other
10 substrate and the cured material of the fluorine-containing monomer.

Prior Art

One-sided or two-sided pressure-sensitive adhesive tape is used by peeling off the releasing paper or releasing film at the time of use. The widely generally used releasing
15 film is comprised of a biaxially oriented polyethylene terephthalate film coated with an agent containing mainly silicone which can form a low energy surface.

Releasing films treated on their surfaces with silicone as a releasing agent are being used by preference in a broad range of fields, but there is a demand for releasing films to take the place of these in fields such as hard disk drives and other computer components, semiconductors, and electrical and electronic circuits and components where there is an
20 extreme aversion to the deposition of contaminants since polydimethylsiloxane, silicone ring monomers, silicone oligomers or the like become contaminants.

Fluorine-containing polymers are known as low surface free energy polymers with extremely low surface free energy. Fluorine-containing polymethacrylates or fluorine-
25 containing polyacrylates also have low surface free energy as described in R. Ramharack and T.H. Nguyen, *J. Poly. Sci.: Part C Polymer Letters*, 25, 93-98 (1987). As substances with low surface free energy, there are polyethylene (about 31 dyne/cm), polydimethylsiloxane (about 21 dyne/cm), polytetrafluoroethylene (about 19 dyne/cm), etc., but polyfluorinated acrylate has a surface energy in the range of about 10 to 25
30 dyne/cm (changing depending on length of side chain or end group) and therefore has an extremely low surface free energy even among low surface free energy substances.

Therefore, if a releasing sheet using polyfluorinated acrylate could be provided, an extremely useful releasing sheet with a surface energy lower than before and further not containing silicone could be expected.

On the other hand, as examples of application of electron beams to releasing sheets, as shown in U.S. Patent No. 5,037,668 (Nagy), a method is disclosed of obtaining releasability by introducing a powder of polytetrafluoroethylene in acrylate. Evans et al. (U.S. Patent No. 4,533,566) shows that the adhesion between silicone and a polyester film is improved by irradiation by an electron beam. U.S. Patent No. 4,985,473 or Japanese Unexamined Patent Publication (Kokai) No. 57.16067 (Williams et al.) shows a coating agent with a releasing effect containing a fluorine-containing polymethacrylate or fluorine-containing polyacrylate. However, this is intended for a releasing force of 115 to 725 g/cm². Since the amount of fluorine contained is small, it is not suited for the object of the present invention. Pacansky et al. show that it is possible to form a low surface free energy film by curing fluoroacrylate and a diacrylate of perfluoropolyether by an electron beam (*Progress in Org. Coatings*, 18, 79-87 (1990)).

U.S. Patent No. 5,811,183 (Shaw et al.) discloses how to produce a releasing material by curing a silicone-based or fluorine-containing acrylate thinly vapor deposited on a substrate by electron beams or UV rays or other radiation. This method is a vapor deposition method using heating in vacuum and is not a solution coating method, so requires an extremely complicated apparatus. Further, the radiation uses UV rays or low accelerating voltage electron beams to cure the silicone-based or fluorine-containing acrylate and is controlled so as not to lower the peeling strength or tensile strength of paper as the substrate. Usually, a paper liner is not used in the field of the electronic and the electronics where contaminations should be severely prevented, since fine fiber chips leaving from ends of the paper become contaminations.

Japanese Unexamined Patent Publication (Kokai) No. 3-250034 discloses how to add an oligomer or polymer to a fluorine-containing acrylate monomer to raise the viscosity and thereby reduce the repellency of the monomer and to cure the same by irradiation by electron beams. This is not suited to a releasing sheet however. Further, since a fluorine-containing acrylate monomer solution to which an oligomer or polymer is added is cured by an electron beam, the wettability of the fluorine-containing acrylate

mixture and substrate is not improved. The wettability is the matter of interface tension (Nippon Adhesive Association "Adhesive Handbook (2nd)", p. 20, 1971). Further, the predetermined chemical bond prescribed in the present invention is not formed between the fluorine-containing acrylate cured material and the substrate.

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Problem to be Solved by the Invention

As explained above, no releasing sheet obtained by coating and curing a fluorine-containing acrylate or other low surface energy fluorine-containing monomer and superior in adhesion between the substrate and cured fluorine-containing polymer has been demanded.

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It is possible to cause a polyfluorinated acrylate to cure on a polyester film or the like, but the adhesion between the substrate and the polyfluorinated acrylate is extremely low, the adhesion is not satisfactory for practical use, and when the pressure-sensitive adhesive tape is laid over the surface of the cured fluorinated acrylate, held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours, then the pressure-sensitive adhesive tape is peeled off to test the adhesion between the substrate and polyfluorinated acrylate, the polyfluorinated acrylate layer easily ends up peeling off and therefore this is not practical as a releasing sheet.

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Therefore, an object of the present invention is to provide a practical releasing sheet having a coating of a cured layer of the material of a low surface energy fluorine-containing monomer such as a polyfluorinated acrylate.

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Means for Solving the Problem

According to the present invention, it was discovered that if a compound for decreasing the interface tension with the substrate surface is added to a fluorine-containing monomer having a surface tension of not more than 25 dyne/cm for coating the surface of a substrate such as a polyester film or if a specific substrate is used to improve the coatability (wettability) of the fluorine-containing monomer with the substrate and the surface of the substrate is irradiated by an electron beam and the electron beam is irradiated under predetermined conditions, the irradiation by the electron beam causes at least the surface of the substrate to be activated and radicals to be produced and a chemical

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bond formed between the substrate and the fluorine-containing monomer, the chemical bonding force can be strengthened so that there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent. This property was tested in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after
5 being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours, and in this way it is possible to provide a releasing sheet coated with a cured material of a low surface energy fluorine-containing monomer having practical adhesion with the substrate.

According to the present invention, the following are provided:

(1) A fluorine-containing releasing sheet comprising a substrate and a releasing
10 layer coated on said substrate,

said releasing layer being a cured material layer of a composition comprising a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm and 0.05 to 20% by weight of a coatability-improving agent which reduces the interfacing tension between said fluorine-containing monomer and said
15 substrate, and

said releasing layer has a fluorine content of not less than 50% by weight.

(2) A fluorine-containing releasing sheet as set forth in (1), wherein said fluorine-containing releasing sheet has a chemical bond between said releasing layer and said substrate, the bonding force of the chemical bond being a bonding force by which
20 there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

(3) A fluorine-containing releasing sheet as set forth in (1) or (2), wherein said
25 coatability-improving agent is at least one type selected from a fluorine-containing oil having a functional group, a fluorine-based surfactant, a hydrofluorocarbon, and a hydrocarbon-based acrylate.

(4) A fluorine-containing releasing sheet as set forth in (1) (2) or (3), wherein
30 said coatability-improving agent is a hydrofluorocarbon used as a solvent for said fluorine-containing monomer.

(5) A fluorine-containing releasing sheet as set forth in (2) to (4), wherein said-chemical bond between said releasing layer and said substrate has a bonding force by which there is no transfer of the releasing agent to a pressure-sensitive adhesive contacting the releasing agent for even one piece in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 110°C for 7 hours

(6) A fluorine-containing releasing sheet as set forth in any one of (1) to (5), wherein the peeling strength at room temperature of the releasing layer is not more than 50 g/inch.

(7) A fluorine-containing releasing sheet comprising a substrate and a releasing layer coated on said substrate, said substrate having at least a surface of a halogen-containing polymer, an olefin-based polymer, a polyvinyl acetate, or a copolymer containing the same, and said releasing layer being a cured material of a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm.

(8) A fluorine-containing releasing sheet as set forth in (6), wherein said fluorine-containing releasing sheet has a chemical bond between said releasing layer and said substrate, the bonding force of the chemical bond being a bonding force by which there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent in a cross cut tape test for 25 pieces-cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

(9) A fluorine-containing releasing sheet as set forth in (8), wherein said cured fluorine monomer further contains at least one type of coatability-improving agent selected from a fluorine-containing oil having a functional group, a fluorine-based surfactant, a hydrofluorocarbon, and a hydrocarbon-based acrylate.

(10) A process of production of a fluorine-containing releasing sheet comprising:

coating a substrate with a composition comprising a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm and

0.05 to 20% by weight of a coatability-improving agent which reduces the interfacing tension between said fluorine-containing monomer and said substrate and

irradiating the obtained substrate coated with the fluorine-containing monomer with an electron beam to cure the fluorine-containing monomer and form a chemical bond between the cured material of the fluorine-containing monomer and said substrate.

(11) A process of production of a fluorine-containing releasing sheet as set forth in (10) wherein said irradiation by the electron beam is performed at an accelerating voltage of at least 50 keV and an amount of irradiation in the range of 3 to 100 Mrad and under conditions whereby the bonding force between the cured material layer of the fluorine-containing monomer and said substrate is one where there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

(12) A process of production of a fluorine-containing releasing sheet comprising:

coating a substrate having at least a surface of a halogen-containing polymer, an olefin-based polymer, a polyvinyl acetate, or a copolymer containing the same, with a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm and

irradiating the obtained substrate coated with the fluorine-containing monomer with an electron beam to cure the fluorine-containing monomer and form a chemical bond between the cured material layer of the fluorine-containing monomer and said substrate.

(13) A process of production of a fluorine-containing releasing sheet as set forth in (12), wherein said irradiation by the electron beam is performed at an accelerating voltage of at least 50 keV and an amount of irradiation in the range of 3 to 100 Mrad and under conditions whereby the bonding force between the cured material layer of the fluorine-containing monomer and said substrate is one where there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the cured material in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

(14) A process of production of a fluorine-containing releasing sheet comprising the steps of irradiating a substrate with an electron beam to cause the production of radicals on the surface of said substrate, coating said substrate with radicals present at its surface with a composition comprising a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm and 0.05 to 20% by weight of a coatability-improving agent which reduces the interfacing tension with said substrate, and thereby forming a chemical bond between the surface of the substrate and the composition, and

curing the composition coated on the substrate by radiation.

(15) A process of production of a fluorine-containing releasing sheet as set forth in (16), wherein said irradiation by the electron beam is performed at an accelerating voltage of at least 50 keV and an amount of irradiation in the range of 3 to 100 Mrad and under conditions whereby the bonding force between the cured material layer of the fluorine-containing monomer and said substrate is one where there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

(16) A process of production of a fluorine-containing releasing sheet comprising the steps of:

irradiating a substrate having at least a surface of a halogen-containing polymer, an olefin-based polymer, a polyvinyl acetate, or a copolymer containing the same, with an electron beam to cause the production of radicals on the surface of said substrate,

coating said substrate with radicals present at its surface with a composition comprising a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm, and

curing the fluorine-containing monomer coated on the substrate by radiation, whereby forming a chemical bond between the surface of the substrate and the cured material of the fluorine-containing monomer.

(17) A process of production of a fluorine-containing releasing sheet as set forth in (16), wherein said irradiation by the electron beam is performed at an accelerating voltage of at least 50 keV and an amount of irradiation in the range of 3 to 100 Mrad and

under conditions whereby the bonding force between the layer of the cured material of the fluorine-containing monomer and said substrate is one where there is no transfer of a releasing agent to the pressure-sensitive adhesive side in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

According to the releasing sheet of the present invention, it is possible to prevent to an extreme extent deposition of silicone as a contaminant in hard disk drives and other computer components, semiconductors, and electrical and electronic components. Due to this, the invention may be used in fields where there is an extreme aversion to contamination or as a coating agent or laminate requiring non-adhesiveness and prevention of contamination.

BRIEF DESCRIPTION OF THE DRAWINGS

[Fig. 1] shows a releasing sheet comprising a substrate 1 coated with a layer of fluorine-containing monomer cured material 2.

[Fig. 2] shows a releasing sheet comprising a substrate 1 with a primer surface layer 3 coated with a fluorine-containing monomer cured material 2.

[Fig. 3] shows the state of peeling off a releasing sheet 5 from a pressure-sensitive adhesive tape 6.

Mode of Working the Invention

The releasing sheet of the present invention includes both what are ordinarily called sheets and films.

The substrate of the releasing sheet of the present invention includes polyesters (in particular polyethylene terephthalate, isophthalate, copolyester etc.), polyolefins (in particular polyethylene etc.), polyethylene naphthalate, polyimide, paper, etc. and is not particularly limited. The invention of the present application however is particularly effective in the case of substrates of a nature difficult to be wet by a fluorine-containing monomer. Preferred substrates of the releasing sheet are polyester-based and polyethylene.

The substrates generally used for releasing sheets are normally inferior in adhesion with polyfluorine-containing acrylate and other fluorine-containing polymers, so up to now

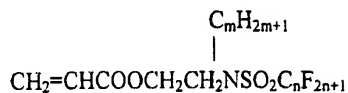
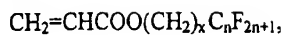
no releasing sheet obtained by coating and curing a fluorine-containing acrylate or other low surface energy fluorine-containing monomer and superior in adhesion between the substrate and the cured fluorine-containing polymer has been demanded.

5 The releasing layer formed by coating on the substrate of the releasing sheet of the present invention is a cured material of a compound obtained by using a fluorine-containing monomer having a surface tension of not more than 25 dyne/cm, more preferably not more than 20 dyne/cm, still more preferably not more than 18 dyne/cm. When using a mixture of fluorine-containing monomers, it is preferable that all of the fluorine-containing monomers have the above surface tensions, but it is also possible for
10 the surface tension of the mixture to be in the above range.

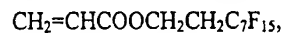
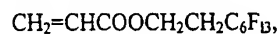
As the fluorine-containing monomer of the present invention, use may be made of a electron-beam curable monomer which includes in its molecule an ethylene unsaturated bond and contains at least 50% by weight of fluorine, preferably at least 60% by weight.

A typical example of such a fluorine-containing monomer is a fluorine-containing
15 acrylate, for example, a fluorine-containing acrylate such as shown by the general formula:

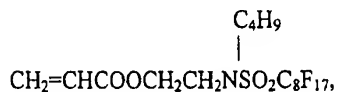
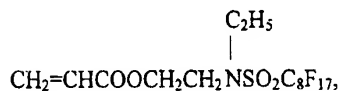
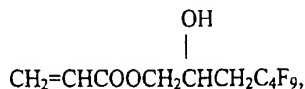
Chemical 1



where x is 1 - 5, preferably 1 or 2, n is 3 - 12, preferably 5 - 9, and m is 0 - 4, preferably 1 or 2. In general, as described in U.S. Patent No. 2,642,416 (Ahlbrecht et al.), this is synthesized by condensation of a perfluoroalkyl group-containing alcohol and acrylic acid ($\text{CH}_2=\text{CHCOOH}$). Here, the number of carbon atoms n is 3 to 12, preferably 5 to 9, the number of carbon atoms m is 0 to 4, preferably 1 or 2, and x is 1 to 5, preferably 1 or 2. Specifically, mention may be made of



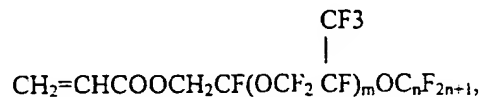
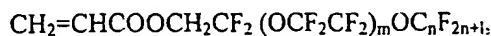
Chemical 2



etc.

Further, as the fluorine-containing acrylate containing perfluoroether, mention may be made of a fluorine-containing acrylate such as shown by the general formula:

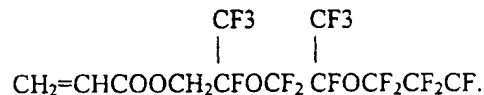
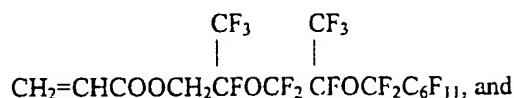
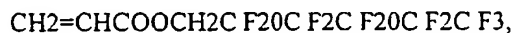
Chemical 3



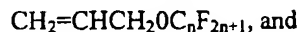
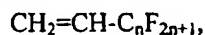
(in these formulae, $m = 1 - 20$, preferably $1 - 5$, $n = 1 - 20$, preferably $1 - 10$)

specifically

Chemical 4

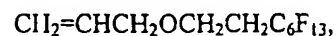
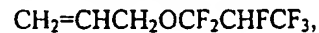
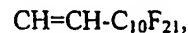


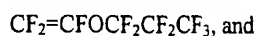
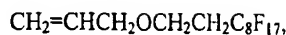
As monomers other than fluorine-containing acrylates, mention may be made of ethylene-based and acryl-based fluorine-containing monomers such as those of the general formulas:



(in these formulae, $n = 1 - 20$, preferably $1 - 10$, and $m = 1 - 20$, preferably $1 - 5$)

specifically mention may be made of:





5 The fluorine-containing acrylate referred to in the present invention also includes a corresponding fluorine-containing methacrylate if curable by an electron beam.

Further, mixtures of the fluorine-containing monomer may be used in the present invention.

10 The fluorine-containing monomer of the present invention does not include silicone. A fluorine-based releasing sheet can prevent to an extreme extent the deposition of silicone as a contaminant in hard disk drives and other computer components, semiconductors, and electrical and electronic components, so may be used in fields where there is an extreme aversion to contamination or as a coating agent or laminate requiring non-adhesiveness and prevention of contamination.

15 The present invention discloses first that it is necessary to coat the surface of the substrate well (wet it) with a fluorine-containing monomer in order to cause the resulting cured material comprising a fluorine-containing monomer such as a fluorine-containing acrylate having a low surface tension to strongly adhere to the substrate. If the wettability (coatability) of the fluorine-containing monomer to the substrate is poor, the coating
20 becomes uneven, a thin and uniform coating cannot be obtained and the adhesive force is inferior, and as a result there are the problems of unevenness in the peeling strength as well, exposure of the substrate, and increase of the peeling strength. Further, there is the problem that the coating process itself is difficult and the monomer ends up coagulating shortly after being coated on the substrate. Further, if the wettability is poor, the adhesion
25 obtained between the monomer and the substrate is also inferior even when next activating the surface of the substrate by an electron beam.

The present inventors discovered that a fluorine-containing monomer has a poor wettability with a substrate of a polyester etc.

30 According to conventional knowledge, if the surface tension of a liquid is larger than the surface tension of a solid, the liquid cannot be wet on the surface of the solid. Therefore, to coat a liquid having a surface tension larger than the surface tension of a

solid on the surface of that solid, a surfactant for lowering the surface tension with the solid is added to the liquid. On the other hand, it is known that compounds which in themselves have low surface tensions such as silicone can wet various substrates well.

In the process of studies for the formation of coating of a fluorine-containing polymer on a substrate of a polyester etc., however, the present inventors discovered that a fluorine-containing monomer has an inferior wettability (coatability) with respect to a substrate of a polyester etc. despite having an extremely low surface tension. Further, they found that the cause of the difficulty of the fluorine-containing monomer wetting a substrate is the overly large interfacing tension at the interface of the two and were able to improve the wettability (coatability) of the fluorine-containing monomer with the substrate by adding to the fluorine-containing monomer a compound decreasing the interface tension, not a compound reducing the surface tension of the monomer as in the past.

According to the *Setchaku Handbook (Adhesion Handbook)* (Japan Adhesion Association ed., 2nd edition, p. 44, Nikkan Kogyo Shimbunsha, Tokyo, 1971), it is stated that the interfacing tension between a solid and a liquid should be reduced as much as possible to enhance the adhesive force between the solid and liquid and that simultaneously this increases the adhesive force by bringing the critical surface tension (γ_c) of the solid and the surface tension (γ) of the liquid close to each other.

In this way, the present invention, as described above, has as its first characteristic feature the improvement of the wettability (coatability) between a fluorine-containing monomer and the substrate. Therefore, it adds to the fluorine-containing monomer a coatability-improving agent so as to reduce the interfacing tension between the fluorine-containing monomer and substrate or selects a specific substrate for use.

Reduction of the interfacing tension of the fluorine-containing monomer is possible by adjusting the type and the amount of the coatability-improving agent. The amount of the coatability-improving agent added is in the range of 0.05 to 20% by weight, preferably from 0.1 to 15% by weight. If the amount of the coatability-improving agent added is less than 0.05% by weight, the interfacing tension between the fluorine-containing monomer and the substrate will not sufficiently decrease. If the amount of the coatability-improving agent added exceeds 20% by weight, the low surface energy (releasing capability) of the fluorine-containing monomer will be diluted or inhibited. Further, it is preferred that the

additive has the fluorine group and hydrocarbon group be held in the same molecule to improve the affinity between the fluorine-containing monomer and the substrate.

According to the present invention, while not limited to this, the following compounds may be added:

5 First, a hydrofluorocarbon (HFC) may be used as the solvent. A chlorofluorocarbon-based solvent (CFC) has a high ozone destructive potential (ODP), so use is restricted, but if an HFC is used, it is possible to coat the fluorine-containing monomer evenly on the substrate without destroying the ozone layer. The HFC used as a solvent is almost completely removed at the time of drying if it has a low boiling point, but
10 remains residually in the coated fluorine-containing monomer layer and reduces the interfacing tension between the fluorine-containing monomer layer and substrate. In other words, since an HFC has both a hydrocarbon group and fluorine group, its solubility with a fluorine-containing monomer and affinity with the substrate are improved.

As the HFC which can be used here, mention may be made of a hydrofluoroether (HFE), a compound of the general formula R_f-O-R or the general formula R_f-R (in which
15 formulas, R_f is a linear or branched perfluoroalkyl group and R is a linear or branched alkyl group), or a solvent having both a hydrocarbon-group and fluorine group. Preferably, there are $C_4F_9OCH_3$, $C_4F_9OC_2H_5$, $C_5H_3F_7$, $C_4F_9C_2H_5$, $CF_3CFHCH_2CF_2CF_3$, etc. If having a high boiling point, it may be added as a surfactant. For example, this may be obtained as
20 HFE-7100, HFE-7200 (both trademarks, made by 3M), Vertrel (trademark, made by DuPont), Zeorora H (trademark, made by Nippon Zeon), etc.

When using an HFE as a solvent, the fluorine-containing monomer may be coated as a solution with a concentration of about 0.1 to 50% by weight in the HFE and dried.

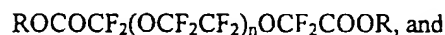
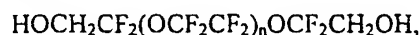
Second, a fluorine-containing oil having a hydroxy group, ester group, carboxy
25 group, or other functional group, in particular having a hydroxy group, may be used. The fluorine-containing oil means a fluorine-containing compound of oligomer or polymer which is a liquid at room temperature, particular perfluoropolyether. A fluorine-containing oil having a functional group not only enables the interfacing tension with the substrate to be reduced, but also can react with the fluorine-containing monomer by radiation.

30 As opposed to this, as a perfluoroether based fluorine-containing oil having a perfluoropolyether terminal fluorinated by fluorine gas treatment etc. and having no

functional group, there are generally known for example Krytox (trademark) of DuPont, Formblin (trademark) of Ausimont, Demnum (trademark) of Daikin, etc., but the surface tension of these fluorine-containing oils of a perfluoropolyether base not having functional groups is a low one equal to that of a fluorine-containing monomer and the coatability is poorer than that of a fluorine oil containing a functional group.

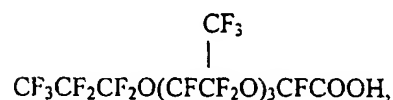
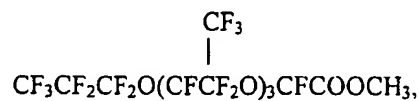
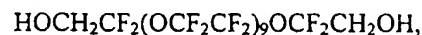
As a fluorine oil having a functional group which can be used here, there are the fluorine oils having functional groups such shown by the general formulas:

Chemical 5



wherein n is 0 - 50, preferably 3 - 20 in these formulae, specifically

Chemical 6

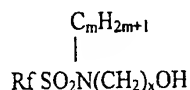
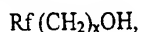


etc. Further, fluorine oils having functional groups are commercially available as the DISOC (isocyanate group), DIAC (carboxy group), DOL (hydroxy group), and DEAL (ester group) of the Formblin (trademark) series of Ausimont and the FC-2022 of the Dynamar (trademark) series of 3M (functional groups indicated in parentheses above).

Third, it is possible to use a fluorine-based surfactant for the fluorine-containing monomer.

As a fluorine-based surfactant able to be used here, there is the Fluorad (trademark) series sold by 3M, for example, FC-430, FC-740, etc. These fluorine-based surfactants were developed as surfactants for addition to hydrocarbons or silicone to lower their interface tension as described in M.T. Pike, *Fluorochemical Surfactant, Paint and Varnish Production*, March, 27-32 (1972), but if added to a fluorine-containing monomer according to the present invention, the wettability of the fluorine-containing monomer and substrate is improved despite the action of hydrocarbon groups and hydrophilic groups thereof. Further, as other nonionic surfactants, there are fluorine-based surfactants having hydroxy groups and nonionic surfactants such as shown by the general formulas:

Chemical 7



where x is 1 - 5, preferably 1 or 2, m is 0 - 4, preferably 1 or 2, Rf is $\text{CF}_3(\text{CF}_2)_n$.

where n is 1 - 12, preferably 6 - 10.

Further, there are fluorine-containing ester based surfactants generally synthesized by a condensation reaction between a fluorine compound having a hydroxy group and a carboxylic acid and ones shown by the general formula RfCOOR , specifically, $\text{C}_6\text{F}_{13}\text{COOCH}_2\text{CH}_3$, $\text{C}_8\text{F}_{17}\text{COOCH}_2\text{CH}_3$, $\text{C}_6\text{F}_{13}\text{COOCH}_3$, $\text{C}_8\text{F}_{17}\text{COOCH}_2\text{CH}_3$, etc.

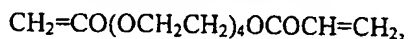
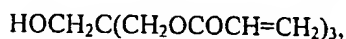
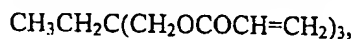
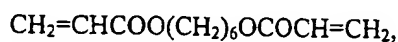
The fluorine-based surfactant added to the fluorine-containing monomer may be added in an amount of 0.01 to 10% by weight with respect to the fluorine-containing monomer.

Fourth, a small amount of a hydrocarbon based monomer, in particular an acrylate, may be used with the fluorine-containing monomer. Acrylates can be easily mixed with each other even if containing fluorine and hydrocarbons.

In this case, by selecting the amount of the monomer added, it is possible to obtain the advantage of an increase in the coagulating force of the cured fluorine-containing monomer polymer layer without increasing the peeling strength with the pressure-sensitive

agent too much. The amount of the hydrocarbon-based monomer added should be determined in consideration of the desired peeling strength, coatability, cost, coagulating force, etc., but in general not more than 20% by weight is preferable with a fluorine-containing acrylate.

5 As the hydrocarbon-based monomer able to be used for this purpose, there is for example an acrylate expressed by the general formula $\text{CH}_2=\text{CHCOOR}$. Further, if there are two or more acryl groups, it may be used as a crosslinking agent. Specifically, there are:



etc.

15 Other than acrylates, there are compounds having allyl groups, for example, triallyl isocyanate (TAIC), triallyl cyanurate (TAC), etc.

These coatability-improving agents for adjusting the interface tension between the above fluorine-containing monomers and the substrate can be used separately or in combination.

20 In the present invention, the surface tensions of the fluorine-containing monomer and the substrate are known. Further, as described in the Adhesive Science Committee ed., *Sechaku: Riron to Oyo (Adhesion: Theory and Application)*, pp. 74-77, Tokyo, Maruzen (1965), the surface tension may be measured by known methods such as the optical reflection method, image method, slanted plate method, drop formation method, capillary rise method, and Wilhelmy method. Further, the surface tension of the
25 composition of the fluorine-containing monomer and coatability-improving agent can also be measured by the same methods.

30 In the present invention, a coatability-improving agent is added to the fluorine-containing monomer as described above. In the composition, in order to be able to keep the superior releasing property of the fluorine-containing monomer, the amount of the fluorine-containing monomer should be at least 80% by weight, preferably at least 85% by

weight, more preferably at least 90% by weight. It is also possible to bring the content close to substantially 100% by weight.

The releasing layer of the present invention realizes superior properties by adding just a coatability-improving agent, i.e., without addition of an oligomer or polymer to the fluorine-containing monomer, but if necessary a coupling agent or other additive may be added in a suitable quantity to an extent not detracting from the effect of the present invention. For example, the coupling agent may be 2-methacryloxyethyl trimethoxy silane, 3-acryloxypropyl trimethoxy silane, 3-methacryloxypropyl trimethoxy silane, vinyltrimethoxysilane, vinyltriethoxysilane, γ -aminopropyltrimethoxysilane, and N- β (aminoethyl) γ -aminopropyl methyl dimethoxysilane.

Further, in the present invention, it was discovered that even when not adding a compound for adjusting the interface tension to the fluorine-containing monomer, the fluorine-containing monomer can be coated well if the substrate has at least a surface comprised of a halogen-containing polymer, an olefin based polymer, a polyvinyl acetate, or copolymers containing the same. A mixture containing these polymers may be used. The amount of these polymers in the mixture may be in a range of 5 - 100% by weight.

It would be expected from the above discoveries of the present invention that an excellent wettability with the fluorine-containing monomer would not be obtained, but surprisingly an extremely good wettability is exhibited. "Has at least a surface comprised of a halogen-containing polymer, an olefin-based polymer, a polyvinyl acetate, or copolymers containing the same" means that the substrate is comprised of a halogen containing polymer, an olefin-based polymer, a polyvinyl acetate, or copolymers of the same or the surface of the substrate is treated by a halogen-containing polymer, an olefin-based polymer, a polyvinyl acetate, or copolymers of the same.

When using a halogen-containing polymer (for example PVDC), an olefin-based polymer, a polyvinyl acetate, or a copolymer of the same as a primer, as described in U.S. Patent No. 4,863,801, the primer is superior in wettability with polyester film and a fluorine-containing monomer can be coated uniformly over the same. If a fluorine-containing monomer is coated on such a primed substrate and irradiated with an electron beam in accordance with the present invention, while the primer is inherently superior in

adhesion with the substrate, a predetermined chemical bond of the present invention is formed between the cured fluorine-containing monomer and the primer.

The thickness of the coating of the PVDC or other primer should be about 1 μm .

When using these substrates, the fluorine-containing monomer can be coated well by itself, but as explained above it is also possible to add a compound for adjusting the interfacing tension to the fluorine-containing monomer.

According to the present invention, when adopting any of the above methods and coating the fluorine-containing monomer on the substrate, it is possible to improve the wettability of the fluorine-containing monomer with the substrate. As described in "Adhesion Handbook" supra. p. 20, the wettability, i.e., excellent coatability of a fluid on a substrate is a primary requirement extremely important to adhesion. As a result, when irradiating the surface of the substrate with an electron beam, the chemical bonding force between the cured layer of the fluorine-containing monomer and the substrate can be made the desired value or more; the peeling strength of the required characteristic of the releasing sheet is the extremely low peeling strength of the fluorine-containing polymer as it is since the coating is based substantially on the fluorine-containing monomer; and there is no drop in performance due to uneven coating.

The releasing sheet of the present invention has the fluorine-containing monomer coated on the substrate in the above way cured by irradiation by an electron beam. It is known that a fluorine-containing monomer cures if irradiated by an electron beam. It has not been known up to now however that if the fluorine-containing monomer is coated on the substrate after being adjusted in interfacing tension and the conditions are controlled for the irradiation by an electron beam, it is possible to produce a releasing sheet having the desired adhesion between the cured material of the fluorine-containing monomer and the substrate. Japanese Unexamined Patent Publication (Kokai) No. 3-250034 discloses adding an oligomer or polymer to a fluorine-containing acrylate monomer to raise the viscosity and thereby reduce the repellency of the monomer and curing by irradiation of an electron beam, but not only is this not directed to a releasing sheet, but also in the conventional method of coating and drying a polymer having a fluorinated group to obtain a coating of the polymer on a substrate by deposition, to eliminate the use of the now prohibited chlorofluorocarbon-based solvents, the fluorine-containing acrylate monomer

solution containing the oligomer or polymer is cured by the electron beam, so the interfacing chemistry of the wettability of the fluorine-containing acrylate cured member and Substrate is not considered. Further, this does not disclose anything regarding the formation of the predetermined chemical bond defined in the present invention by an electron beam between the fluorine-containing acrylate cured member and the substrate. With simple irradiation by an electron beam in this way for the purpose of causing a fluorine-containing monomer to cure, the adhesion of the cured material of the fluorine-containing monomer with the substrate is low.

As opposed to this, in the present invention, looking at the fluorine-containing monomer layer coated as explained above on the substrate, the fluorine-containing monomer layer coated on the substrate is not simply cured. Rather, it was discovered that by irradiating the surface of the substrate by a powerful electron beam so as to activate the surface of the substrate by the electron beam and cause the production of radicals on the surface of the substrate and causing a chemical reaction between the radicals on the surface of the substrate with the fluorine-containing monomer or the radicals produced from there to positively form a chemical bond (covalent bond), it is possible to make the chemical bonding force stronger than conventionally expected, therefore provide a highly useful and practical releasing sheet with a low surface energy, superior releasing fluorine-containing polymer strongly adhered to the substrate, and further obtain a process of production which is relatively simple industrially and superior in economy.

Further, according to the present invention, there is provided a releasing sheet having a fluorine-containing releasing coating layer with a chemical bond (covalent bond) present between the fluorine-containing monomer cured layer and the substrate formed by irradiation by an electron beam and having a chemical bonding force by which there is little transfer of a releasing agent to a pressure-sensitive adhesive in contact with the releasing agent. This property was tested in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours. More preferably, it is possible to provide a fluorine-containing monomer based releasing sheet free from transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent for even one piece in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held

at a temperature of 110°C for 7 hours. It is also possible to realize a bond able to withstand further tougher conditions by optimization of the conditions. This cross cut tape test may be performed in accordance with the procedure defined in JIS-K-5400.

Looking at the strong chemical bond between the cured fluorine-containing monomer layer and substrate of the present invention, it is possible to obtain one having a bonding force satisfying the requirements of the present invention not only by the method of formation by irradiation by an electron beam after coating the fluorine-containing monomer on the substrate as explained above, but also by the method of first irradiating the surface of the substrate by an electron beam to activate the surface of the substrate and then coating the fluorine-containing monomer on the activated surface of the substrate and curing by UV rays (or electron beams), though the chemical bonding force tends to be inferior to that of the former method.

The thickness of the fluorine-containing monomer layer formed on the substrate is preferably small so long as the desired coating strength and peeling strength are obtained, but in general is about 0.005 to 50 μm in terms of the thickness after curing by an electron beam, more preferably 0.1 to 5 μm or so. If thinner than 0.005 μm , the result is uneven, while if thicker than 50 μm , the result is uneconomical.

The releasing agent of the releasing sheet of the present invention is a fluorine-containing polymer having an extremely low surface energy, preferably a fluorine-containing polyacrylate. Since it is possible to substantially avoid use of or minimize any ingredient inhibiting the peeling strength, it is possible to make the peeling strength extremely small. The peeling strength of the releasing sheet of the present invention can be made not more than 50 g/inch, more preferably not more than 30 g/inch, measured at room temperature in accordance with the method described in U.S. Patent No. 4,567,073. Further, it is possible to realize, for example, a strength of the releasing force at room temperature of not more than 100 g/inch, more preferably not more than 50 g/inch, measured after a laminate of the releasing sheet and the a pressure-sensitive tape is heat treated at 110°C for 7 hours.

The releasing sheet of the present invention can as explained above be produced by coating a substrate well with a fluorine-containing monomer by treatment with a specific compounding agent or primer, then irradiating the fluorine-containing monomer layer with

an electron beam. The coating method may be, for example, bar coating, wire bar coating, Meyer bar coating, four roll coating, gravure coating, spray coating, notch bar coating and die coating. The irradiation by the electron beam however must be under conditions making the above chemical bonding force one where there is no transfer of a releasing agent to the pressure-sensitive adhesive side in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours. While depending on the substrate and the coated fluorine-containing monomer layer, in general the irradiation may be performed by suitably selecting the accelerating voltage of the electron beam to at least 50 keV, more preferably at least 100 keV, and the amount of the electron beam to 3 to 100 Mrad, more preferably 5 to 30 Mrad. If the accelerating voltage is less than 50 keV, it is not possible to cure the fluorine-containing monomer and realize the desired chemical bonding force with the substrate. If the amount of the electron beam is less than 3 Mrad, the fluorine-containing monomer is not sufficiently cured, while if over 100 Mrad, undesirable degradation of the substrate is caused.

The electron beam should be irradiated while lowering the concentration of oxygen in an inert atmosphere as much as possible. Preferable adhesion is obtained if the concentration of oxygen is not more than 1000 ppm. The best results are obtained with the minimum possible concentration of oxygen. Lowering the concentration of oxygen to substantially not more than 5 ppm however is not economical. If the concentration of oxygen is high, the surface activated by the electron beam will sometimes become oxidized. Depending on the type of the pressure-sensitive adhesive, it may not be possible to obtain the desired low surface energy of the fluorine-containing monomer cured layer.

When pretreating the surface of the substrate by an electron beam and then coating the fluorine-containing monomer and curing it by UV rays (or an electron beam), the conditions for the pretreatment by the electron beam may be basically the same as explained above. It is necessary, however, to coat the fluorine-containing monomer in a period of time during which the radicals remain after pretreating the surface of the substrate by an electron beam and to control the concentration of oxygen in the atmosphere at that time. The atmosphere may be an inert atmosphere, for example, nitrogen or rare gas. When the fluorine-containing monomer is cured after some of the fluorine-containing

monomer form chemical bonds, with radicals on the surface of the substrate, the cured material of the fluorine-containing monomer has chemical bonds with the substrate.

Figure 1 shows a releasing sheet comprising a substrate having a coating of a fluorine-containing monomer cured material, while Fig. 2 shows a releasing sheet comprised of a substrate treated on its surface with a primer and having a coating of the fluorine-containing monomer cured material. In the figures, 1 is a substrate, 2 a fluorine-containing monomer cured layer, and 3 a primer layer. Figure 3 shows the peeling of a pressure-sensitive adhesive tape 6 protected by the releasing sheet 5 of the present invention from the releasing sheet.

The content of fluorine of the releasing layer in the present invention is at least 50% by weight, preferably at least 60% by weight, more preferably at least 65% by weight. If less than 50% by weight, the releasing performance falls.

Examples

The present invention will be explained next by using examples. Unless specifically indicated to the contrary, the concentrations and percentages are all percentages by weight.

Example 1

10% by weight of Dynamar FC-2202 (perfluoropolyether diol, fluorine content about 62%, made by 3M) was added as a coatability-improving agent to Viscoat 17F ($\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_8\text{F}_{17}$, molecular weight 486.17, fluorine content 66.4%, made by Osaka Yuki Kagaku Kogyo) to prepare a coating solution. The solution was measured for surface tension γ by a platinum plate using a Kyowa Surface Tension Measurement Device Model A-3 (Wilhelmy method, made by Kyowa Kagaku). To examine the coatability of the solution, a No. 3 rod wire was used to coat a 0.05 mm thick biaxially oriented polyethylene terephthalate film (Lumilar, untreated, made by Toray) and the wettability after coating but before irradiation was observed. The results are shown together in Table 1.

Example 2

The same procedure was performed as in Example 1 except for adding perfluoropolyether diol ($\text{HOCH}_2\text{CF}_2(\text{OCF}_2\text{CF}_2)_9\text{OCF}_2\text{CH}_2\text{OH}$, molecular weight about 1200, fluorine content 62%, indicated as "Diol" in Table 1) instead of the coatability-improving agent FC-2202 of Example 1. The results are similarly shown in Table 1.

Example 3

The same procedure was performed as in Example 1 except for adding KAYARAD HDDA ($\text{CH}_2=\text{CHCOO}(\text{CH}_2)_6\text{OCOCH}=\text{CH}_2$ molecular weight 226.27, fluorine content 0%, made by Nihon Kayaku) instead of the coatability-improving agent FC-2202 of Example 1. The results are similarly shown in Table 1.

Example 4

The same procedure was performed as in Example 1 except for adding HFE-7100 ($\text{CF}_3\text{CF}_2\text{OCH}_3$ molecular weight 234.06, fluorine content 73%, made by 3M) instead of the coatability-improving agent FC-2202 of Example 1. It was confirmed that the coating layer contained HFE-7100 in an amount of more than 0.05% after the drying. The results are similarly shown in Table 1.

Example 5

The same procedure was performed as in Example 4 except for making the amount of the coatability-improving agent HFE-7100 of Example 4 added 30% by weight. It was confirmed that the coating layer contained HFE-7100 in a small amount of more than 0.05% by weight after the drying. The results are similarly shown in Table 1.

Example 6

The same procedure was performed as in Example 1 except for making the amount of the coatability-improving agent HFE-7100 of Example 1 added 1% by weight. The results are similarly shown in Table 1.

Example 7

The same procedure was performed as in Example 1 except for adding 0.05% by weight of Fluorad FC-430 (fluorine-based surfactant, fluorine content about 15%, made by 3M) instead of the coatability-improving agent ' FC-2202 of Example 1. The results are similarly shown in Table 1.

Example 8

The surface tension γ of Viscoat 17F ($\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_8\text{F}_{17}$, made by Osaka Yuki Kagaku Kogyo) was measured by a platinum plate using a Kyowa Surface Tension Measurement Device Model A-3 (Wilhelmy method, made by Kyowa Kagaku). To examine the coatability of the solution, a rod wire was used to coat a film obtained by treating a polyethylene terephthalate film with polyvinylidene chloride (PVDC) and the wettability was observed. The results are shown together in Table 1. Further, the data of the surface tension γ_c of the PVDC is also shown in Table 2.

Comparative Example 1

The same procedure was performed as in Example 1 except for not adding the coatability-improving agent FC2202 of Example 1. The results are similarly shown in Table 1.

Comparative Example 2

The same procedure was performed as in Example 1 except for adding Demnum S-20 (perfluoropolyether, average molecular weight 2700, fluorine content about 69%, made by Daikin) as a fluorine-containing oil with no functional group instead of the coatability-improving agent FC-2202 of Example 1. The results are similarly shown in Table 1.

Comparative Example 3

The same procedure was performed as in Comparative Example 2 except for adding Krytox 143AB (perfluoropolyether, fluorine content about 69%, made by DuPont) as a fluorine-containing oil with no functional group instead of the Demnum S-20 of Comparative Example 2. The results are similarly shown in Table 1.

Comparative Example 4

The same procedure was performed as in Example 1 except for making the amount of the coatability-improving agent FC-430 of Example 7 added 0.001%. The results are similarly shown in Table 1.

Example 9

The same procedure was performed as in Example 8 except for using AC600 ($\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_6\text{F}_{15}$, molecular weight 386.16, fluorine content 64%, made by Clariant) instead of the Viscoat 17F of Example 8. The results are shown in Table 2.

Example 10

The same procedure was performed as in Example 8 except for using PPTVE (2-perfluoropropoxy)perfluoropropyl trifluorovinyl ether, molecular weight 432.06, fluorine content 70.4%, made by Tokyo Kasei Kogyo) instead of the Viscoat 17F of Example 8.

The results are shown in Table 2.

Example 11

The same procedure was performed as in Example 8 except for using a film of PVDF (Kynar 740, polyvinylidene fluoride, made by Tokyo Kasei Co.) as the substrate instead of the PVDC of Example 8. The results are shown in Table 2.

Example 12

The same procedure was performed as in Example 8 except for using a film of PVC (polyvinylchloride) as the substrate instead of the PVDC of Example 8. The results are shown in Table 2.

Example 13

The same procedure was performed as in Example 8 except for using a film of a polymer blend of PVDF and PMMA (blending ratio of PVDF/PMMA = 80/20) (Denka DX film, made by Denki Kagaku Kogyo) as the substrate instead of the PVDC of Example 8. The results are shown in Table 2.

Example 14

The same procedure was performed as in Example 8 except for using PP (polypropylene film) as the substrate instead of the PVDC of Example 8. The results are shown in Table 2.

5

Example 15

The same procedure was performed as in Example 8 except for using LLDPE (linear low density polyethylene film) as the substrate instead of the PVDC of Example 8. The results are shown in Table 2.

10

Example 16

The same procedure was performed as in Example 8 except for using PVAC (polyvinyl acetate film) as the substrate instead of the PVDC of Example 8. The results are shown in Table 2.

15

Comparative Example 5

The same procedure was performed as in Example 8 except for using PET (polyethylene terephthalate film, made by Toray) as the substrate instead of the PVDC of Example B. The results are shown in Table 2.

20

Example 17

10% by weight of Dynamar FC-2202 (perfluoropolyether diol, made by 3M) was added as a coatability-improving agent to Viscoat 17F ($\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_8\text{F}_{17}$, made by Osaka Yuki Kagaku Kogyo) to prepare a coating solution. The coating solution was coated using a rod wire on a 0.05 mm thick biaxially oriented polyethylene terephthalate film (Lumilar, made by Toray). The coating thickness was about 5 μm . A 15 Mrad electron beam was irradiated at an accelerating voltage of 150 kV at room temperature with nitrogen substitution (10 to 50 ppm concentration of oxygen). For the electron beam irradiation device, an Electron Curtain System 7824 made by Energy Sciences Inc. was used. The line speed was 2 m/min.

30

Next, the adhesion between the coating layer and substrate of the irradiated sample was evaluated. The releasing performance was tested. In accordance with JISK-5400, cuts were made at 2 mm pitch from the coating layer side of the releasing material. A 3M 4395 tape (acryl-based one-sided pressure-sensitive adhesive tape) was adhered from above this and a load of 20 g/cm² was applied at 70°C for 24 hours for aging. After the aging, the assembly was cooled to the room temperature or 23°C, then the 4395 tape was peeled off at 180° at a tensile speed of 300 mm/min. No peeling of the substrate and coating layer was observed. Further, in accordance with JIS-K-5400, cuts were made at 2 mm pitch from the coating layer side of the releasing material. A 3M 4395 tape (acryl-based one-sided pressure-sensitive adhesive tape) was adhered from above this and aging was performed with no load at 110°C for 7 hours for aging. After the aging, the assembly was cooled to the room temperature, then the 4395 tape was peeled off at 180° at a tensile speed of 300 mm/min. These test results are shown together in Table 3.

Example 18

The same procedure was performed as in Example 17 except for adding 0.05% by weight of Fluorad FC-430 (fluorine-based surfactant, made by 3M) instead of the 10% by weight of Dynamar FC-2202 as the coatability improving agent of Example 17. The results are shown in Table 3.

Example 19

The same procedure was performed as in Example 17 except for adding 30% by weight of HFE7100 (made by 3M) instead of the 10% by weight of Dynamar FC-2202 as the coatability-improving agent of Example 17 and using a film obtained by treating a polyethylene terephthalate film by polyvinylidene chloride (PVDC) as the substrate instead of the polyethylene terephthalate film. The results are shown in Table 3.

Comparative Example 6

1% of a photoinitiator (Darocur 1173, made by Ciba Specialty Chemicals K.K.) was added to Viscoat 17F (CH₂=CHCOOCH₂CH₂C₈F₁₇, made by Osaka Yuki Kagaku Kogyo) The solution was coated using a rod wire on a 0.05 mm thick biaxially oriented

polyethylene terephthalate (PET) film (LUMILAR, made by Toray). Another PET film was laid above this then the assembly was cured by UV rays. The UV irradiation was performed at about 2000 mJ/cm². After the curing, one of the two PET films was peeled off by hand to obtain a releasing film comprised of a PET film and coating layer. The adhesion was evaluated in the same way as in Example 17. The results are shown in Table 3.

Table 1

	Fluorine Monomer	Additive/Amount Added (%)		Fluorine content	Substrate	Surface Tension of coating material γ (dyne/cm)	Wettability (appearance)
Ex. 1	17F	FC-2202	10	66	PET	14.2	Good
Ex. 2	17F	Diol	10	66	PET	14.1	Good
Ex. 3	17F	HDDA	10	59	PET	18.0	Good
Ex. 4	17F	HFE-7100	10	67	PET	13.6	Good
Ex. 5	17F	HFE-7100	30	68	PET	14.6	Good
Ex. 6	17F	HFE-7100	1	66	PET	13.3	Good
Ex. 7	17F	FC-430	0.05	66	PET	13.4	Good
Ex. 8	17F	--	0	66	PVDC-PET	12.8	Good
Comp. Ex. 1	17F	--	0	66	PET	12.8	Poor
Comp. Ex. 2	17F	Demnum S-20	10	67	PET	12.8	Poor To fair
Comp. Ex. 3	17F	Krytox 143A B	10	67	PET	12.9	Poor To fair
Comp. Ex. 4	17F	FC-430	0.00 1	66	PET	12.8	Poor To fair

Note 1) Wettability: "Poor" indicates cissing, "Fair" indicates some cissing, "Good" indicates good wettability.

Note 2) 17F: $\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{C}_8\text{F}_{17}$

Note 3) In Examples 4 and 5, HFE-7100 was used as a solvent and dried after coating, but it was confirmed that HFE-7100 remained in the coating in a small amount of more than 0.05% by weight.

Table 2

	Fluorine Monomer	Substrate	Critical Surface Tension of Substrate γ_c (dyne/cm)	Wettability (appearance)
Ex. 8	17F	PVDC	40	Good
Ex. 9	15F	PVDC	40	Good
Ex. 10	PPTVE	PVDC	40	Good
Ex. 11	17F	PVDF	25	Good
Ex. 12	17F	PVC	39	Good
Ex. 13	17F	PVDF/PMMA = 80/20	28	Good
Ex. 14	17F	PP	29	Good
Ex. 15	17F	PE	31	Good
Ex. 16	17F	PVAC	30	Good
Comp. Ex. S	17F	PET	43	Poor

Wettability: "Poor" indicates cissing, "Fair" indicates some cissing, "Good" indicates good wettability.

PPTVE: $\text{CF}_3\text{CF}_2\text{CF}_2\text{OCFCF}_2\text{OCF} = \text{CF}_2$

Table 3

	Fluorine monomer/coatability improving agent/ substrate	Source of radiation	Peeling Strength (g/Inch)	Cross cut tape test (peeled pieces/25 pieces)	
				70°C, 24 hr	110°C 7 hr
Ex. 17	17F/FC-2202/PET	EB	10-20	0/25	17/25
Ex. 18	17F/FC-430/PET	EB	10-20	0/25	24/25
Ex. 19	17F/HFE/PVDC-PET	EB	30	0/25	25/25
Comp. Ex. 6	17F/-/PET	UV	--(1)	25/25	25/25

(1) Measurement not possible due to movement of releasing layer to tape side.

CLAIMS

We Claim:

1. A fluorine-containing releasing sheet comprising a substrate and a releasing layer coated on said substrate,

5 said releasing layer being a cured material layer of a composition comprising a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm and 0.05 to 20% by weight of a coatability-improving agent which reduces the interfacing tension between said fluorine-containing monomer and said substrate, and

10 said releasing layer has a fluorine content of not less than 50% by weight.

2. A fluorine-containing releasing sheet according to claim 1, wherein said fluorine-containing releasing sheet has a chemical bond between said releasing layer and said substrate, the bonding force of the chemical bond being a bonding force by which
15 there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

20 3. A fluorine-containing releasing sheet as set forth in claim 1 wherein said coatability-improving agent is at least one type selected from a fluorine-containing oil having a functional group, a fluorine-based surfactant, a hydrofluorocarbon, and a hydrocarbon-based acrylate.

25 4. A fluorine-containing releasing sheet as set forth in claim 1 wherein said coatability-improving agent is a hydrofluorocarbon used as a solvent for said fluorine-containing monomer.

30 5. A fluorine-containing releasing sheet as set forth in claim 2 wherein said chemical bond between said releasing layer and said substrate has a bonding force by which there is no transfer of the releasing agent to a pressure-sensitive adhesive contacting

the releasing agent for even one piece in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 110°C for 7 hours.

5 6. A fluorine-containing releasing sheet as set forth in claim 1 wherein the peeling strength at room temperature of the releasing layer is not more than 50 g/inch.

 7. A fluorine-containing releasing sheet comprising a substrate and a releasing layer coated on said substrate,
10 said substrate having at least a surface of a halogen-containing polymer, an olefin-based polymer, a polyvinyl acetate, or a copolymer containing the same, and
 said releasing layer being a cured material layer of a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm.

15 8. A fluorine-containing releasing layer according to claim 7, wherein said fluorine-containing releasing layer has a chemical bond between said releasing layer and said substrate, the bonding force of the chemical bond being a bonding force by which there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for
20 24 hours.

 9. A fluorine-containing releasing sheet as set forth in claim 7 wherein said cured fluorine monomer further contains at least one type of coatability-improving agent selected from a fluorine-containing oil having a functional group, a fluorine based
25 surfactant, a hydrofluorocarbon, and a hydrocarbon-based acrylate.

 10. A process of production of a fluorine-containing releasing sheet comprising:
30 coating a substrate with a composition comprising a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm and

0.05 to 20% by weight of a coatability-improving agent which reduces the interfacing tension between said fluorine-containing monomer and said substrate and

irradiating the obtained substrate coated with the fluorine-containing monomer with an electron beam to cure the fluorine-containing monomer and form a chemical bond
5 between the cured material layer of the fluorine-containing monomer and said substrate.

11. A process of production of a fluorine-containing releasing sheet according to claim 10, wherein said irradiation by the electron beam is performed at an accelerating voltage of at least 50 keV and an amount of irradiation in the range of 3 to
10 100 Mrad and under conditions whereby the bonding force between the layer of the cured material of the fluorine-containing monomer and said substrate is one where there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

12. A process of production of a fluorine-containing releasing sheet comprising:

coating a substrate having at least a surface of a halogen-containing polymer, an olefin-based polymer, a polyvinyl acetate, or a copolymer containing the same, with a
20 radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm, and

irradiating the obtained substrate coated with the fluorine-containing monomer with an electron beam to cure the fluorine-containing monomer and form a chemical bond between the cured material layer of the fluorine-containing monomer and said substrate.

13. A fluorine-containing releasing sheet according to claim 12, wherein said irradiation by the electron beam is performed at an accelerating voltage of at least 50 keV and an amount of irradiation in the range of 3 to 100 Mrad and under conditions whereby the bonding force between the layer of the cured material of the fluorine-
30 containing monomer acrylate and said substrate is one where there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent in a cross

cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

14. A process of production of a fluorine-containing releasing sheet
5 comprising the steps of

irradiating a substrate with an electron beam to cause the production of radicals on the surface of said substrate, coating said substrate with radicals present at its surface with a composition comprising a radiation-polymerizable fluorine-containing monomer having a surface tension of not more than 25 dyne/cm and 0.05 to 20% by weight of a coatability-improving agent which reduces the interfacing tension with said substrate, and thereby
10 forming a chemical bond between the surface of the substrate and the composition and curing the composition coated on the substrate by radiation.

15. A process of production of a fluorine-containing releasing sheet
15 according to claim 14, wherein said irradiation by the electron beam is performed at an accelerating voltage of at least 50 keV and an amount of irradiation in the range of 3 to 100 Mrad and under conditions whereby the bonding force between the layer of the cured material of the fluorine-containing monomer and said substrate is one where there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent
20 in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20g/cm² for 24 hours.

16. A process of production of a fluorine-containing releasing sheet
comprising the steps of:

25 irradiating a substrate having at least a surface of a halogen-containing polymer, an olefin-based polymer, a polyvinyl acetate, or a copolymer containing the same, with an electron beam to cause the production of radicals on the surface of said substrate,

coating said substrate with radicals present at its surface with a composition comprising a radiation-polymerizable fluorine-containing monomer having a surface
30 tension of not more than 25 dyne/cm, and

curing the fluorine-containing monomer coated on the substrate by radiation,

whereby forming a chemical bond between the surface of the substrate and the cured material of the fluorine-containing monomer.

17. A process of production of a fluorine-containing releasing sheet
5 according to claim 16, wherein said irradiation by the electron beam is performed at an accelerating voltage of at least 50 keV and an amount of irradiation in the range of 3 to 100 Mrad and under conditions whereby the bonding force between the layer of the cured material of the fluorine-containing monomer and said substrate is one where there is no transfer of a releasing agent to a pressure-sensitive adhesive contacting the releasing agent
10 in a cross cut tape test for 25 pieces cut at 2 mm pitch with a pressure-sensitive adhesive after being held at a temperature of 70°C and a pressure of 20 g/cm² for 24 hours.

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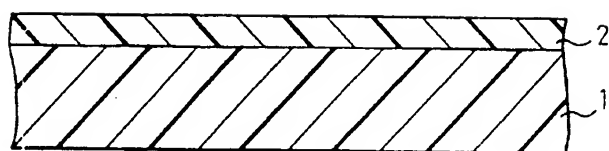


Fig. 1

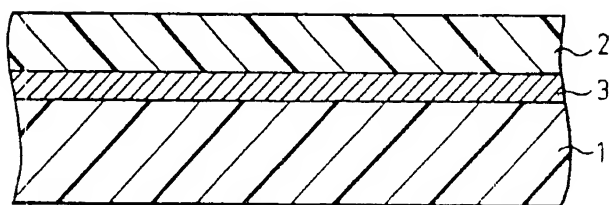


Fig. 2

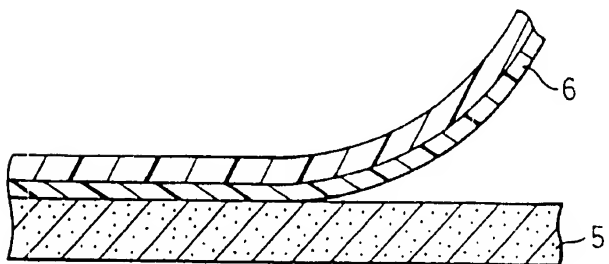


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 00/03625

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D4/00 C09J7/02 B05D3/06 C08J7/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C09J B05D C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	example 1	1-6, 8-17
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

26 May 2000

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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